



# The Patent Office

PCT/GB98/03011

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales

ERU,

09/529159

NP91RH

REC'D 04 NOV 1998

WIPO

PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

G D Court.

Dated

21 OCT 1998

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)



- 8 OCT 1997

The  
Patent  
Office

RECEIVED BY POST

08OCT97 E308274-1 D02776  
P01/7700 25.00 - 9721214.6

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

DERA/HO/COM/IPD01/P2621

2. Patent  
(The Patent)

9721214.6

0 8 OCT 1997

3. Full name, address and postcode of the or of each applicant (underline all surnames)

The Secretary of State for Defence  
Defence Evaluation and Research Agency  
DERA Farnborough  
Farnborough, Hants GU14 OLX

Patents ADP number (if you know it)

2576002

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

54 51 0012

4. Title of the invention

Smectic Liquid Crystal Devices

5. Name of your agent (if you have one)

J B Edwards

~~J B Edwards~~  
~~D/IPR~~ Formalities Section

"Address for service" in the United Kingdom to which all correspondence should be sent

Mr A O Bowdery et al  
D/IPR(DERA) Formalities  
Poplar 2  
MOD(PE) Abbey Wood #19  
PO Box 702  
Bristol BS12 7DU

~~(DERA)~~  
~~Poplar 2~~  
~~MOD(PE) Abbey Wood 19~~  
~~BRISTOL BS34 8JH~~

Richard Anthony Lawrence  
Hewlett-Packard Limited  
Intellectual Property Section  
Filton Road, Stoke Gifford  
Bristol BS34 8QZ

Patents ADP number (if you know it)

807P

2576002

7448038001

29603003

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number or earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See note (d))

## Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form none

Description 20

Claim(s) 2

Abstract 1

Drawing(s) 3

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77) 1

Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I / We request the grant of a patent on the basis of this application.

Signature



Date 01 10 97

12. Name and daytime telephone number of person to contact in the United Kingdom J B Edwards 01684 894234

### Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent of the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

### Notes

- If you need help to fill in this form or have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have attached 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.

# PATENT APPLICATION SMECTIC LIQUID CRYSTAL DEVICES

5 Inventors:

John Clifford Jones

Guy Peter Bryan-Brown

Ian Charles Sage

All of DERA Malvern

10 St Andrew Road  
Malvern. Worcs. WR14 3PS

File Ref: DERA/HO/COM/IPD01/P2621

15 Filed: .....1997

## Slippery Surfaces cases:

- 1 (P2618)general case genslip.1 - cover all the following file on same day
- 20 2 (P2619)bistable case - bislip1.doc was pat4 etc involves HP
3. (P2620)twisted nematic tnslip1.doc improves TN devices was pat5 etc
- 4 (P2621)ferro electric - feslip1.doc improves FELCDs

## SMECTIC LIQUID CRYSTAL DEVICES

This invention relates to smectic liquid crystal devices, for example ferroelectric liquid crystal devices, devices (e.g. displays) with improved contrast and brightness.

5 antiferroelectric liquid crystal devices, smectic liquid crystal devices, electroclinic liquid crystal devices; electro-optic shutters, spatial light modulators, and displays.

Liquid crystal devices typically comprise of a thin layer of a liquid crystal material contained between cell walls. Optically transparent electrode structures on the walls  
10 allow an electric field to be applied across the layer causing a re-ordering of the liquid crystal molecules.

There are three known types of liquid crystal material nematic, cholesteric and smectic each having different molecular ordering. The present invention concerns devices  
15 using smectic materials.

There are a number of devices based on smectic liquid crystal materials including:

### A: Ferroelectric liquid crystals (usually SmC\*).

20

One example of this is bistable and is often termed surface stabilised FLC devices (SSFLC) ref. N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett., 36, 899 (1980). In this device planar aligned surfaces are arranged with parallel or anti parallel preferred alignment directions. The device is cooled from an overlying Smectic A phase into a  
25 bookshelf arrangement of the smectic layers, that is the material forms into micro layers arranged normal to the cell walls as in books on a shelf.

In the original patent, the device used an unrubbed polymer surface alignment treatment to ensure the liquid crystal director  $n$  lies preferentially and substantially  
30 parallel to the surface plane (i.e.  $\perp$  to  $s$ , the surface normal). A preferred direction was then imparted by heating to the smectic A phase and shearing the layers in the required

direction. The layers remained fixed on cooling into the SmC\* phase. The surface energy is minimum for  $n \perp s$  so that two minimum energy states occur which can be selected by suitable DC electric field.

- 5 Bradshaw and Raynes realised that improved SmA alignment for such a device resulted by having a chiral nematic N\* phase above the SmA in which the pitch was sufficiently long for the surface forces to cause unwinding of the spontaneous helicity for a significant temperature range above the transition. They also required that the surface should be pre-treated to impart the preferred directions, often by use of parallel  
10 or antiparallel rubbing of a polyimide or polyamide layer; GB-2.210.469 USP-4.997.264. GB-2.209,610. USP-5.061.047. GB-2.210.468.

Later it was found that when a bookshelf aligned (where the layer normal is parallel to the plane of the device i.e.  $\delta=0$ ) SmA sample is cooled into the SmC\* phase, the layers  
15 become tilted in a chevron type of configuration: two type of chevron can exist and are defined as C<sub>1</sub> and C<sub>2</sub> type (ref J.Kambe et al Ferroelectrics (1991) vol 114. pp3). This has been ascribed to the combined effect of shrinkage of the smectic layer spacing and pinning of the layers at the surface. The resulting chevron structure means that the director in the middle of the cell is (roughly) fixed in one of two orientations  
20 significantly less than the full cone angle. This means that with no applied field there is a substantial drop in the angle between the optic axis of the two "surface stabilised" states which leads to a corresponding drop of the display brightness. A number of methods of improving the optical brightness have been proposed for practical devices:

25 1 AC field stabilisation:

An applied AC field pulse of insufficient time and voltage ( $\tau$  V) to latch into the two states couples to the dielectric tensor (primarily the dielectric biaxiality) to increase the angle between these states and enhance the brightness. The main problem with this type of approach is that a high frequency voltage is required constantly to maintain the  
30 required brightness. This causes a high power dissipation, particularly for complex displays where the applied frequency is high. Usually the brightness is compromised

by using a suitably low AC voltage. It has the advantage that, if C2U type alignment is used, there is no need for surface switching, and hence surface memory effects are minimal, and the slower switching at the surface does not effect the device.

5    2        High pre-tilt Parallel:

This geometry has (approximately) the same chevron structure with the director at the chevron interface also at a low angle to the rubbing direction. However, the director at the surface is at a much higher in-plane twist angle due to the competing effects of  
10    lying on the SmC\* cone and with the preferred alignment pre-tilt. This type of device gives good brightness but suffers from a slower response since it involves surface switching, and from strong surface memory problems which may lead to image sticking.

15   3        Quasi-bookshelf:

Two methods may be used to reduce the layer tilt angle and thereby increase the device brightness. Pre-treating the device with a low frequency field of sufficient magnitude or choosing certain materials in which the layer shrinkage on cooling  
20    through the smectic phases is reduced (some materials may actually increase layer spacing on cooling). Such a device has similar advantages and disadvantages to the high pre-tilt configurations.

4        Uniform Tilted layer (High pre-tilt anti-parallel) geometry:

25

Similar to previous two geometry's but there is no chevron (and therefore no constraint on the director at the cell centre) and the high angle between the bistable states is stabilised solely by the surfaces.

30



B: Electro-clinic optical shutters:

Application of a DC field to the smectic A (or other orthogonal smectic) phase of a chiral material leads to an induced tilt of the director and hence optical axis normal to the applied field. In a (approximately) planar aligned liquid crystal cell with electrodes on the substrate surfaces the electroclinic effect induces a rotation of the optic axis by an angle proportional to the applied field  $E$ . Thus, an optical shutter with full analogue amplitude or phase modulation may be obtained.

A common problem with such a device is obtaining suitably uniform and planar alignment of the smectic layers. A lesser problem is that the induced switching may involve some rotation of the director away from the preferred alignment direction at the surface. This movement is subject to a surface viscosity which may impede the switching time of the device and also to certain surface memory effects.

15

C: Anti-ferroelectric smectic liquid crystals (AFLC):

Certain materials form an anti-ferroelectric phase which may be used in active matrix or direct drive devices. Effectively these devices have a similar appearance to the smectic A phase until sufficient DC voltage is applied, above which the sample is in either of two states (depending on the polarity of the applied signal) similar to the normal ferroelectric phase.

There is a limited number of materials which form this phase (particularly over a wide temperature range) and all those found so far have direct isotropic to smectic phase (i.e. no overlying chiral nematic phase). This means that the materials are more difficult to align, forming batonnets (see Gray and Goodby book) of the smectic at this transition.

30

The mechanism for this is that the smectic layer structure nucleates in a limited number of "cold spots" in the isotropic liquid. The layers then curve around this point to minimise the bend and splay of the layer normal. Where the layers meet the surface they become pinned and difficult to move. Hence, it is difficult to obtain the desired layer arrangement (e.g. planar or bookshelf) once the batonnet structure has pre-formed. On cooling into the AFLC phase, the applied field tends to induce twist of the director at the surfaces which also leads to problems associated with surface switching such as slower speed, surface memory effects, etc.

10 D: SmC\* Optical Shutters:

Bradshaw and Raynes also described a type of device in which the FLC is obtained from cooling directly from the unwound N\* phase in a parallel rubbed device, preferably with an applied DC field applied during the phase transition. The unwound N\* phase has the director in the rubbing directions and on cooling into the SmC\* this orientation is maintained and the layer normal twists through the angle  $\theta$ . Degeneracy of the direction in which the layer normal is oriented is removed by the application of the DC field.

20 This is a monostable device, since it always relaxes back to the surface stabilised state (with  $n \parallel s$ ) once the field is removed (it may be used in devices when the field is retained, either through AC stabilisation or through inclusion of TFTs or similar non-linear electrical elements at each pixel. However, it is fast (due to Ps). Primarily switching occurs in the bulk of the cell and little or no switching occurs at the surface.

25 However, this means that the director is highly twisted and non uniform structure. This means that the optical appearance is poor (particularly if used in conjunction with a dye as done in early Hitachi work) and so this is a case where surface switching is required to improve performance. Also, alignment is difficult over a wide temperature range because layer shrinkage still occurs in many N-SMC\* materials, leading to a

30 chevron structure and associated defects.

According to this invention, problems in the above devices may be reduced by use of a surfactant to lower the interaction between the surface(s) of cell wall(s) and the liquid crystal in the smectic phase, or in the overlying nematic phase from which the cell is cooled into the smectic phase for all operating temperatures. This use of a surfactant may be termed a slippery surface treatment. Thus improved alignment, optical properties, switching speed and stability to shock of smectic devices are achieved through slippery surface treatment.

10 According to this invention a smectic liquid crystal device comprises:

a liquid crystal cell including a layer of smectic liquid crystal material contained between two walls bearing electrodes and surface treated to give both an alignment and a surface tilt to liquid crystal molecules:

15

#### CHARACTERISED BY

means for reducing anchoring energy at the surface alignment on one or both cell walls.

20

The means for reducing anchoring energy may be an oligomer containing esters, thiols, and/or acrylate monomers and or which is either spread on the surface or added to the liquid crystal material.

In its most elemental form the surfactant provides a slippery surface which reduces the interaction between the liquid crystal molecules and those of the surface of the cell wall (or alignment layer surface). Thus, the slippery surface may be thought as having increased freedom for translational and rotational movement of the liquid crystal molecules closest to the surface. There are five surface terms (ref: Int Ferroelectric Liquid Crystal Conf (FLC95), Cambridge, UK, 23-27 July 1995, vol.178 No.1-4 J.C.Jones, pp155-165) which are relevant and may be controlled by the surfactant:

(1)  $\alpha$ , zenithal anchoring energy. How easily the director surface tilt angle is changed (i.e. a rotational energy).

(2)  $\beta$ , azimuthal anchoring energy - case of changing surface twist angle of director (i.e. a rotational energy)

(3)  $\gamma$ , related to the pretilt angle of the director at the surface

(4) Layer pinning term - How easily layers may be moved across the surface (i.e. a translational energy). This is the macroscopic effect of the (partial) adsorption of liquid crystal molecules onto the surface layer reducing translational movement of the molecules and hence of the smectic layers.

(5) Polar surface energy - In ferroelectrics (or flexoelectrics) a term which is minimum for a particular orientation of the Ps at the surface.

In the present invention each of these factors is influenced by the presence of a slippery surfactant which acts to separate the solid and liquid crystal regions by the induced changes of liquid crystal order close to the surface. For example, if nematic order exists close to the surface layer of a smectic device, then layer pinning is greatly reduced. If the cone angle is lower surface switching is reduced as

will the polar surface term.

Advantages provided by the present invention:

- 5 (1) Reduced layer pinning hence control of the smectic layers is easier:
- (2) Reduced nematic-like surface energies. hence orientation changes of the director at the surface are enhanced.
- (3) Reduced adsorption of liquid crystal molecules at the surface. hence reduced surface memory effects and reduced surface viscosity;
- 10 (4) Reduced polarity of the surface. hence less coupling to the spontaneous polarisation coefficient ( $P_s$ ) in ferro electric liquid crystal systems resulting in less T state formation.

Brief description of drawings.

15

The invention will now be described. by way of example only with reference to the accompanying drawings of which:-

Figure 1 is a diagrammatic view of a bistable ferro electric display with row and  
20 column drivers providing an x.y matrix display:

Figure 2 is a cross section of the display cell of Figure 1:

Figure 3 is a schematic view of a layer of ferro electric liquid crystal material. showing  
25 two alignment configurations. the  $C_1$  and the  $C_2$  states:

Figure 4 is a schematic view showing the two switched states of the display of  
Figure 1: and

30 Figure 5 is a graph of memory angle against applied voltage for a cell containing a standard material. and the same material but including a slippery surface additive.

Detailed description of invention.

The display cell 1 shown in Figures 1, 2 comprises two glass walls 2, 3 spaced about  
5 1-6  $\mu\text{m}$  apart by a spacer ring 4 and/or distributed spacers.

Electrode structures 5, 6 of transparent tin oxide are formed on the inner face of both  
walls. These electrodes are shown as row and column forming an X, Y matrix but  
may be of other forms. For example, radial and curved shape for a polar co-ordinate  
10 display, or of segments form for a digital seven bar display, or plain sheet electrodes to  
form an optical shutter.

A layer 7 of smectic liquid crystal material is contained between the walls 2, 3 and  
spacer ring 4.

15  
Polarisers 8, 9 are arranged in front of and behind the cell 1. Row 10 and column 11  
drivers apply voltage signals to the cell. Two sets of waveforms are generated for  
supplying the row and column drivers 10, 11. A strobe waveform generator 12  
supplies row waveforms, and a data waveform generator 13 supplies ON and OFF  
20 waveforms to the column drivers 11. Overall control of timing and display format is  
controlled by a control logic unit 14.

Prior to assembly, the walls 2, 3 are surface treated by spinning on a thin layer of  
polymeric material such as polyimide or polyamide, drying and where appropriate  
25 curing; then buffing with a soft cloth (e.g. rayon) in a single direction  $R_1$ ,  $R_2$ . This  
known treatment provides a surface alignment for liquid crystal molecules. In the  
nematic and cholesteric phases and in the absence of an applied electric field the  
molecules at the surface walls 2, 3 align themselves along the rubbing direction  $R_1$ ,  $R_2$   
and at a pretilt angle  $\xi$  of about e.g.  $2^\circ$  to  $10^\circ$  to the surface.

The surface alignment treatment is arranged to provide the required value of pretilt  $\xi$ . For example the material polyimide ( e.g. Polyimide 32) when rubbed gives a typical pretilt of about  $2^\circ$ ; the actual value depends upon liquid crystal material and the processing. Alternatively, as described in GB-A-2.286: GB-A-2.286.467: GB-A-2.286.894: GB-A-2.2986.893, the cell walls may have formed thereon grating structures which provide a range of pretilt angles and alignment directions. The gratings may be symmetric and/or asymmetric in profile, and shaped to give any desired value of pretilt  $\xi$ , and azimuthal and zenithal anchoring energies  $\beta$ ,  $\alpha$  respectively.

The device may operate in a transmissive or reflective mode. In the former light passing through the device e.g. from a tungsten bulb 15 is selectively transmitted or blocked to form the desired display. In the reflective mode a mirror 16 is placed behind the second polariser 9 to reflect ambient light back through the cell 1 and two polarisers. By making the mirror 16 partly reflecting the device may be operated both in a transmissive and reflective mode.

Pleochroic dyes may be added to the material 7. In this case only one polariser is needed and the layer thickness may typically be  $4\text{-}10\mu\text{m}$ .

If the smectic material 7 is a chiral smectic e.g. smectic C ( $S_C^*$ ) then a bistable device can be made. Such a device is the surface stabilised ferroelectric device (SSFLC) supporting two bistable states which are optically distinct. In a chiral smectic material molecules tend to lie and move along the surface of an (imaginary) cone as shown in Figure 4. When the surface alignment directions R1, R2 are parallel the (z) axis of these cones are parallel to these alignment directions and the molecules lie either side of the axis on the cone surface.

In one switched state D1 the molecules lie on one side of the cone, and in the second bistable state D2 lie on the other side of the cone. The switching is achieved by application of a voltage pulse of appropriate sign and length applied through the electrodes 6, 7 coupling with a spontaneous polarisation coefficient  $P_s$  of the material. The cone angle,  $\theta_c$ , is a function of material parameters. In devices the molecules in their two switched positions D1, D2, do not lie on the extremities of the cone but some small distance away. This means that the angle between the bistable positions is somewhat less than the cone angle, and can be increased a bit by application of an ac voltage signal to the material; this is known as ac stabilisation mentioned above. Ideally the angle between the switched states is  $45^\circ$  because this would allow maximum contrast for the cell when arranged between crossed polarisers 8, 9 with the axis of one polariser along one of the switched directions. This gives a dark state in one switched position and a light state in the other switched position.

The angular distance between the two state is defined as the memory angle,  $\theta_m$  (see N. Itoh et al, Jpn. J. Appl. Phys., **31**, L1089 (1992) ). The optimum memory angle for maximum brightness in the light state is therefore  $45^\circ$ . However most materials possess a memory angle which is much less than  $45^\circ$  and so suffer from loss in brightness.

A weak anchoring treatment can be added to a ferroelectric to increase the memory angle and so improve the display brightness.



### Example of cell preparation.

Alignment surfaces were prepared by spin coating a layer of probomide 32 (Ciba  
5 Geigy) onto ITO coated glass and baking the substrates at 300°C. The surfaces were  
then rubbed in one direction R by a nylon cloth attached to a rotating roller. Finally  
cells were constructed in which the rubbing direction  $R_1$  on one surface was parallel to  
that  $R_2$  on the other. The cell gap (d) was set to 1.1  $\mu\text{m}$  using monodispersed spacer  
beads in the edge seal. Each cell was then filled with ZLI 5014 (Merck) ferroelectric  
10 liquid crystal doped with small percentages of N65. Before filling the N65 was cured  
in a separate cell.

Figure 5 shows the memory angle measured from two cells containing either pure ZLI  
5014, or 4% N65 in ZLI 5014 as a function of applied voltage (50kHz AC). The  
15 results clearly show that the weak anchoring treatment has lead to a significant  
increase in memory angle at all voltages. Therefore the treatment has improved this  
ferroelectric device by increasing the on state transmission between crossed polarisers.  
For example at 5 V, the memory angle has increased from 17.1° to 34.4° which would  
lead to a device which is 3.7 times brighter.

20 Bistable ferro electric devices switch upon receipt of a unidirectional pulse of  
appropriate direction, amplitude, and length. Strobe pulses are applied sequentially  
down the rows, whilst one of two different data pulses are applied to each column.  
Examples of addressing are described in USP-5.497.173, GB-2.232.802: US Serial  
25 No. 07/977.442, GB-2.262.831.

Several other smectic devices may be made with alignment surfaces of the present invention. For examples electro-clinic smectic devices: mono stable ferro electric devices USP-5,061,047, USP-4,969,719, USP-4,997,264, colour change smectic  
5 projection cells USP-5,189,534, GB-2,236,403. The alignment may produce a chevron type C1 or C2 type of smectic micro layer arrangement; or a tilted bookshelf arrangement where rubbing directions on opposite walls are in the same direction, or real bookshelf alignment.

10 Reducing anchoring energy allows small amounts of translational movement to occur in micro layers formed during cooling from isotropic phases to smectic phases.

Reduction of anchoring energy can be applied to various smectic devices as follows:

15 (i). Bookshelf and Quasi-bookshelf with low surface viscosity and no surface memory effects

Most materials used in FLC devices exhibit layer shrinkage on cooling through the SmC\* phase due to the increase of the angle between the molecules and layer normal  
20 on cooling. The tendency for the pinning of the smectic layers at the surfaces then leads to the formation of a chevron structure.

If the pinning energy is sufficiently high to prevent any translational slippage of the layers (i.e. the energy cost associated with layer slippage is much greater than energies  
25 associated with the chevron interface, elastic distortion of the director in the triangular director profile, and the orientational surface energy associated with the director being unable to lie in the preferred alignment direction) the layer shrinking requires that the layers tilt with respect to the surface normal.

If both surfaces have similarly high layer slipping terms then the layers must tilt into a chevron structure which is necessarily symmetric about the central plane of the cell. For typical materials this degree of layer shrinkage is such that the layer tilt angle  $\delta$  is a constant fraction of the smectic cone angle  $\theta$  usually about  $\delta/\theta = 0.85$ . This causes a reduction in the angle between the two bistable states and hence optical contrast in the cell. A higher memory angle may be achieved by lowering  $\delta$  in what is often termed quasi bookshelf geometry. If the layer pinning term is made sufficiently weak (for example a relatively high concentration of the surfactant is used) a bookshelf geometry is obtained i.e.  $\delta = 0$ . If the azimuthal angle  $\beta$  is also made sufficiently low then a uniform director profile is possible in which the two bistable states are at the optimum angle of  $\pm\theta$  to the rubbing direction. The resulting high contrast and brightness of the display is also combined with the other advantages of reduced/no surface memory effects (which would be a problem in other bookshelf devices) and faster response (due to the decoupling of the surface director from the solid surface the surface viscosity becomes equivalent to that of the bulk).

(ii). Chevron with improved memory angle.

This device uses the slippery surfactant at sufficient concentration to lower layer tilt angle in chevron geometry, thereby leading to a higher memory angle and improved brightness for multiplexed devices. However, it may be possible to lower the orientational surface energies without a strong effect on the translation energy (i.e. layer pinning). Thus, the chevron structure would remain to a large extent (i.e.  $\delta$  remains unchanged) but the orientation of the director at the surface would be higher. For no applied AC field the surface twist of the director would approach that of the chevron interface. The optical uniformity of this state (and hence contrast) would be improved. Moreover, the lowered surface energy would increase the angle of the director at the surface with an applied AC field, and thus the brightness of an AC stabilised display will also be enhanced.

(iii). Improving isotropic to smectic transition.

Surfactant allows layers to slip easily over the surface to form energy state (i.e. uniform layers) dictated by orientational properties of the surface alone (i.e. no translational restrictions). Particularly useful also in AFLC where  $N^*$  (cholesteric) phase is usually not apparent, but also in other devices (e.g., FLC) where stringent material requirements prevent the use of an  $N^*$  phase.

10 (iv)..Improved stability to mechanical, triennial or electrical damage of smectic devices.

Disruption of a well aligned smectic sample through mechanical, electrical or thermal shock leads to pinning of the layers at the surface which is difficult to remove, even  
15 though the disrupted state is not the lowest energy state. If the pinning is removed then the system may relax back to this minimum energy state before the disruption.

(v)..Improved high tilt chevron device.

20 High surface pre-tilts are used to ensure that the surface orientation of a FLC device in the chevron geometry approaches the cone angle and hence the memory angle is improved (this is used by CANON and is in Jones. Towler Hughes review). In the unwound  $N^*$  phase the director has a large degree of splay and bend distortion. On cooling into the smectic A phase this bend cannot be supported. due to the presence of  
25 the layers and the distortion is pushed to the surfaces where the director is forced to lie away from the desired pretilt. This may lead to variations in the alignment and hence defects in the  $SmC^*$  phase (until switched this geometry often forms a "sandy texture" on first cooling). Moreover, there may be a plastic change of the pre-tilt caused by the zenithal surface memory effect. This means that when cooled into the  $SmC^*$  phase the  
30 effective pretilt is lowered and the resulting memory angle is reduced somewhat.

With the slippery surfactant, the surface memory is reduced and the pre-tilt remains unchanged. Note, this is an example where the slippery surface technique is used in the nematic phase, but results in improved performance of a smectic device.

5 (vi). Improved Electroclinic and antiferroelectric (AFLC) devices

In both of these devices, director twist is induced by the DC electric field there is a tendency for the smectic layers to shrink. If pinned at the surface the applied field tends to induce layer tilt. (although in contradiction to the requirement that  $E \parallel P_i$ )  
10 which reduces optical appearance through defects, and may also reduce viewing angle since the director may tilt out of the cell plane. With the slippery surfactant, both the director and the layers can move easily across the surface, without surface memory or viscosity effects.

15 (viii). Improved N - SmC device.

Advantages ranging from: reduced tendency to form chevron type structure:  
reduced surface memory; faster surface switching.

20 (viii). Reduced tendency form T state formation in FLC

Due to reduced polar surface interaction. This ensures the good optical and electro-optical properties of any of the above devices (in particular the chevron and bookshelf devices).

25

(ix). Improved alignment of smectic devices.

Treatment prevents defects (for example pitch lines in overlying N\* phase, or C1 state/zig-zags in SmC\*) from become pinned at surface irregularities.

30

The monomer materials used may include the following, which are given only by way of example:

methyl acrylate	propane-1,3-diol diacrylate
ethyl acrylate	butane-1,4-diol diacrylate
propyl acrylate	pentane-1,5-diol diacrylate
butyl acrylate	hexane-1,6-diol diacrylate
pentyl acrylate	heptane-1,7-diol diacrylate
2-methylbutyl acrylate	octane-1,8-diol diacrylate
hexyl acrylate	nonane-1,9-diol diacrylate
heptyl acrylate	decane-1,10-diol diacrylate
octyl acrylate	glycerol triacrylate
nonyl acrylate	trimethylolpropane triacrylate
decyl acrylate	pentaerythritol triacrylate
ethyl hexyl acrylate	pentaerythritol tetraacrylate
methyl methacrylate	di-pentaerythritol hexaacrylate
ethyl methacrylate	ethylene glycol dimethacrylate
propyl methacrylate	1,2-propylene glycol dimethacrylate
butyl methacrylate	propane-1,3-diol dimethacrylate
pentyl methacrylate	butane-1,4-diol dimethacrylate
2-methylbutyl methacrylate	pentane-1,5-diol dimethacrylate
hexyl methacrylate	hexane-1,6-diol dimethacrylate
heptyl methacrylate	heptane-1,7-diol dimethacrylate
octyl methacrylate	octane-1,8-diol dimethacrylate
nonyl methacrylate	nonane-1,9-diol dimethacrylate
decyl methacrylate	decane-1,10-diol dimethacrylate
ethyl hexyl methacrylate	glycerol trimethacrylate
styrene	trimethylolpropane trimethacrylate
ethylene glycol diacrylate	pentaerythritol trimethacrylate
1,2-propylene glycol diacrylate	pentaerythritol tetramethacrylate
	di-pentaerythritol hexamethacrylate

A further class of polymers includes di-thiol/diene polymers prepared by the copolymerisation of difunctional alkenes with difunctional thiols under free radical conditions. Monofunctional and/or polyfunctional alkenes and/or thiols may be incorporated in order to modify the properties of the polymer. for example to reduce the molecular weight of the polymer or to introduce a controlled degree of crosslinking in the polymer. The following materials given by way of example only may be included in polymers suitable for the subject of the invention:

methyl acrylate  
ethyl acrylate  
propyl acrylate  
butyl acrylate  
pentyl acrylate  
2-methylbutyl acrylate  
hexyl acrylate  
heptyl acrylate  
octyl acrylate  
nonyl acrylate  
decyl acrylate  
ethyl hexyl acrylate  
methyl methacrylate  
ethyl methacrylate  
propyl methacrylate  
butyl methacrylate  
pentyl methacrylate  
2-methylbutyl methacrylate  
hexyl methacrylate  
heptyl methacrylate  
octyl methacrylate  
nonyl methacrylate  
decyl methacrylate

styrene  
ethylene glycol diacrylate  
1,2-propylene glycol diacrylate  
propane-1,3-diol diacrylate  
butane-1,4-diol diacrylate  
pentane-1,5-diol diacrylate  
hexane-1,6-diol diacrylate  
heptane-1,7-diol diacrylate  
octane-1,8-diol diacrylate  
nonane-1,9-diol diacrylate  
decane-1,10-diol diacrylate  
glycerol triacrylate  
trimethylolpropane triacrylate  
pentaerythritol triacrylate  
pentaerythritol tetraacrylate  
di-pentaerythritol hexaacrylate  
ethylene glycol dimethacrylate  
1,2-propylene glycol dimethacrylate  
propane-1,3-diol dimethacrylate  
butane-1,4-diol dimethacrylate  
pentane-1,5-diol dimethacrylate  
hexane-1,6-diol dimethacrylate  
heptane-1,7-diol dimethacrylate

ethyl hexyl methacrylate  
ethylene glycol divinyl ether  
1,2-propylene glycol divinyl ether  
propane-1,3-diol divinyl ether  
butane-1,4-diol divinyl ether  
pentane-1,5-diol divinyl ether  
hexane-1,6-diol divinyl ether  
heptane-1,7-diol divinyl ether  
octane-1,8-diol divinyl ether  
nonane-1,9-diol divinyl ether  
decane-1,10-diol divinyl ether  
glycerol trivinyl ether  
trimethylolpropane trivinyl ether  
divinyl benzene  
butane-1,3-diene  
pentane-1,4-diene  
hexane-1,5-diene  
heptane-1,7-diene  
octane-1,7-diene  
nonane-1,8-diene  
decane-1,9-diene  
ethylene glycol dithioglycollate  
1,2-propylene glycol dithioglycollate  
propane-1,3-diol dithioglycollate  
butane-1,4-diol dithioglycollate  
pentane-1,5-diol dithioglycollate  
hexane-1,6-diol dithioglycollate  
heptane-1,7-diol dithioglycollate  
octane-1,8-diol dithioglycollate  
nonane-1,9-diol dithioglycollate  
decane-1,10-diol dithioglycollate

octane-1,8-diol dimethacrylate  
nonane-1,9-diol dimethacrylate  
decane-1,10-diol dimethacrylate  
glycerol trimethacrylate  
trimethylolpropane trimethacrylate  
pentaerythritol trimethacrylate  
pentaerythritol tetramethacrylate  
di-pentaerythritol hexamethacrylate  
ethylene glycol diallyl ether  
1,2-propylene glycol diallyl ether  
propane-1,3-diol diallyl ether  
butane-1,4-diol diallyl ether  
pentane-1,5-diol diallyl ether  
hexane-1,6-diol diallyl ether  
heptane-1,7-diol diallyl ether  
octane-1,8-diol diallyl ether  
nonane-1,9-diol diallyl ether  
decane-1,10-diol diallyl ether  
glycerol triallyl ether  
trimethylolpropane triallyl ether  
di-allyl malonate  
di-allyl succinate  
di-allyl glutanate  
di-allyl hexane-1,6-dicarboxylate  
di-allyl heptane-1,7- dicarboxylate  
di-allyl octane-1,8- dicarboxylate  
di-allyl nonane-1,9- dicarboxylate  
di-allyl decane-1,10- dicarboxylate  
di-allyl undecane-1,11- dicarboxylate  
di-allyl dodecane-1,12- dicarboxylate  
di-allyl phthalate



glycerol trithioglycollate  
trimethylolpropane trithioglycollate  
pentaerythritol trithioglycollate  
pentaerythritol tetrathioglycollate  
di-pentaerythritol hexathioglycollate  
4,4'-thiobisbenzenethiol  
di-allyl iso-phthalate  
di-allyl terephthalate  
ethane dithiol  
propane dithiol  
butane dithiol  
pentane dithiol

hexane dithiol

heptane dithiol  
octane dithiol  
nonane dithiol  
decane dithiol  
undecane dithiol  
dodecane dithiol  
ethylene glycol di-3-  
mercaptopropionate  
1,2-propylene glycol di-3-  
mercaptopropionate  
propane-1,3-diol di-3-  
mercaptopropionate

butane-1,4-diol di-3-mercaptopropionate  
pentane-1,5-diol di-3-mercaptopropionate  
hexane-1,6-diol di-3-mercaptopropionate  
heptane-1,7-diol di-3-mercaptopropionate  
octane-1,8-diol di-3-mercaptopropionate  
nonane-1,9-diol di-3-mercaptopropionate  
decane-1,10-diol di-3-mercaptopropionate  
glycerol tri-3-mercaptopropionate  
trimethylolpropane tri-3-mercaptopropionate  
pentaerythritol tri-3-mercaptopropionate  
pentaerythritol tetra-3-mercaptopropionate  
di-pentaerythritol hexa-3-  
mercaptopropionate

Also commercial polymers from Norland  
and Merck eg Norland 65. Norland 63 and  
Merck MXM035

Claims.

1. A smectic liquid crystal device comprising:

- 5 a liquid crystal cell including a layer of smectic liquid crystal material contained between two walls bearing electrodes and surface treated to give both an alignment and a surface tilt to liquid crystal molecules:

CHARACTERISED BY

10

means for reducing anchoring energy at the surface alignment on one or both cell walls.

2. The device of claim 1 wherein the means for reducing energy is an oligomer or  
15 short chain polymer within the liquid crystal material at the cell walls.

3. The device of claim 1 wherein the means for reducing energy is an oligomer containing esters, thiols, and/or acrylate monomers within the liquid crystal material at the cell walls.

20

4. The device of claim 2 wherein the oligomer or short chain polymer has imperfect solubility in the liquid crystal material.

5. The device of claim 2 wherein the oligomer or short chain polymer has a physical  
25 affinity for the surface of the cell wall.

6. The device of claim 2 wherein the oligomer or short chain polymer retains a substantially liquid like surface at the polymer and liquid crystal material interface

7. The device of claim 2 wherein the oligomer or polymer is substantially non-crystalline within the liquid crystal material.
- 5 8. The device of claim 1 wherein the oligomer or polymer reduces the liquid crystal material order parameter at or adjacent the cell walls.
9. The device of claim 1 wherein the oligomer or polymer changes the phase of the liquid crystal material at or adjacent the cell walls.
- 10 10. The device of claim 1 wherein the liquid crystal material is a chiral smectic material, the alignment directions on the two cell walls are substantially parallel, and the device is a bistable device.
- 15 12. The device of claim 1 wherein the alignment directions on the two cell walls are non parallel.
13. The device of claim 1 wherein the liquid crystal material is a non-chiral smectic material.
- 20 14. The device of claim 1 wherein the liquid crystal material is a smectic A material.
15. The device of claim 1 wherein the alignment is provided by a grating surface.
- 25 16. The device of claim 1 wherein the alignment is provided by a rubbed polymer surface.
17. The device of claim 1 wherein one cell wall has an alignment treatment, the other cell wall has no azimuthal alignment direction, and both cell walls are treated with the
- 30 means for reducing anchoring energy.

Abstract.

Smectic liquid crystal devices are formed by a layer of a smectic liquid crystal material  
5 enclosed between two cell walls, both carrying electrode structures, and one or both  
walls treated to align molecules of the liquid crystal material. Most alignment  
treatment give alignment and surface pretilt with a strong azimuthal and zenithal  
anchoring energy to contacting liquid crystal molecules. The invention improves the  
performance of smectic devices by use of a surfactant to lower the interaction and  
10 anchoring energy between the surfaces of the cell walls and the liquid crystal in the  
smectic phase. The reduction of anchoring energy is achieved by an oligomer or short  
chain polymer which is either spread on the surface or added to the liquid crystal  
material. The polymer may be formed by polymerisation of reactive low molecular  
weight materials in solution in the liquid crystal fluid. Typically up to about 10% of  
15 an oligomer is added to the liquid crystal material and cured: either in the cell after  
filling, or prior to installation in the cell. Various types of smectic devices may be  
provided; e.g. bistable ferro electric devices, electro clinic devices, and antiferro  
electric devices.

Fig. 1.

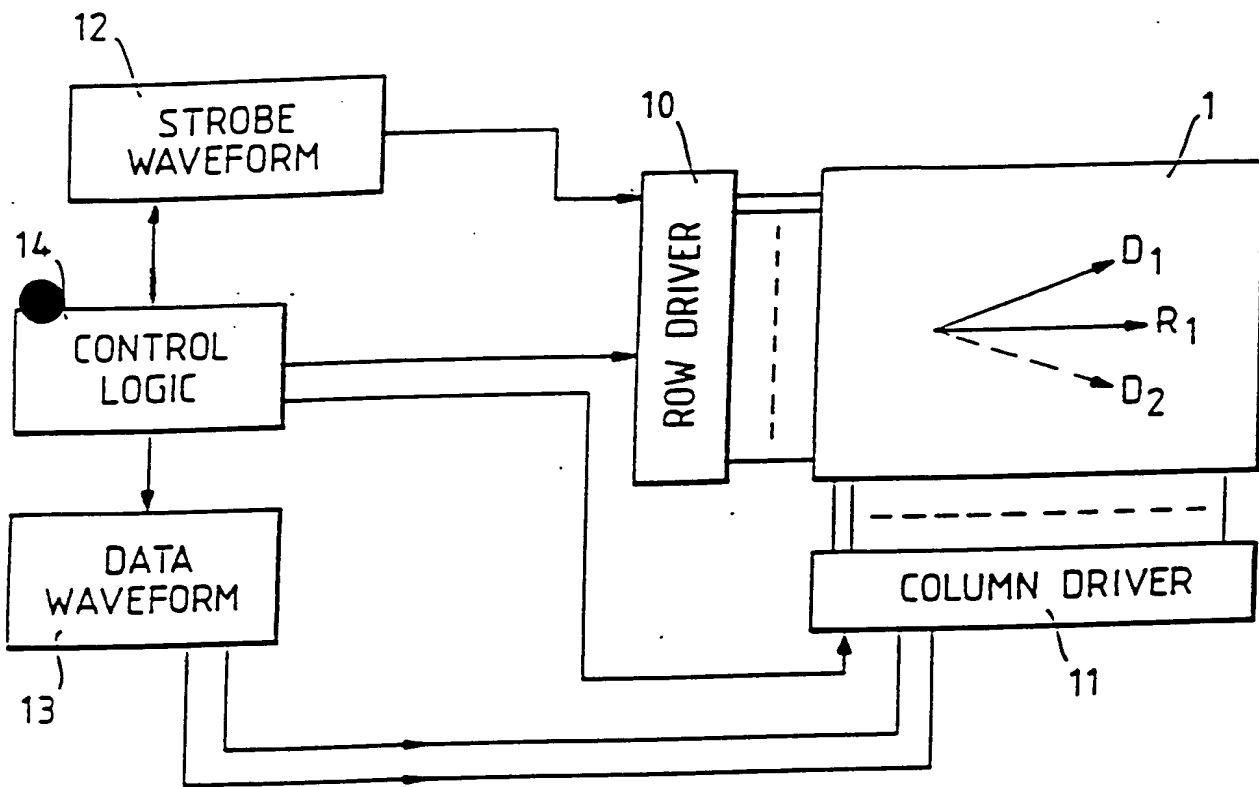
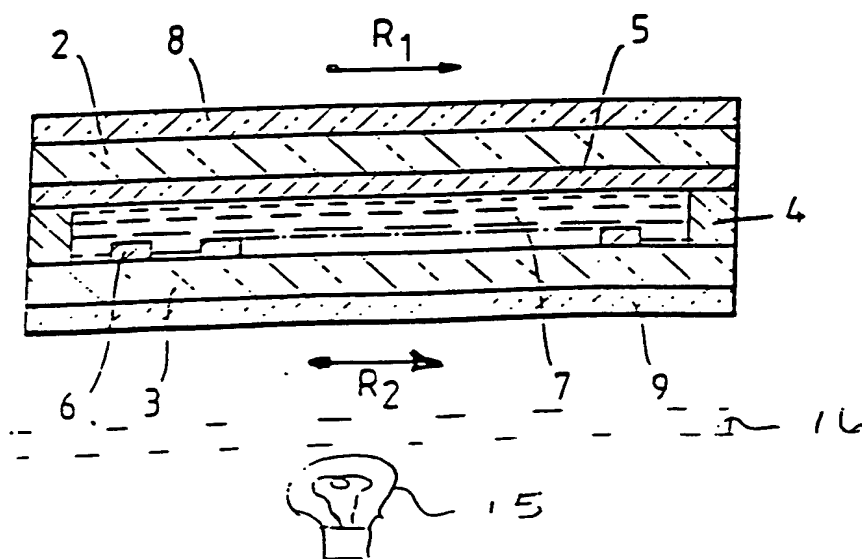


Fig. 2.





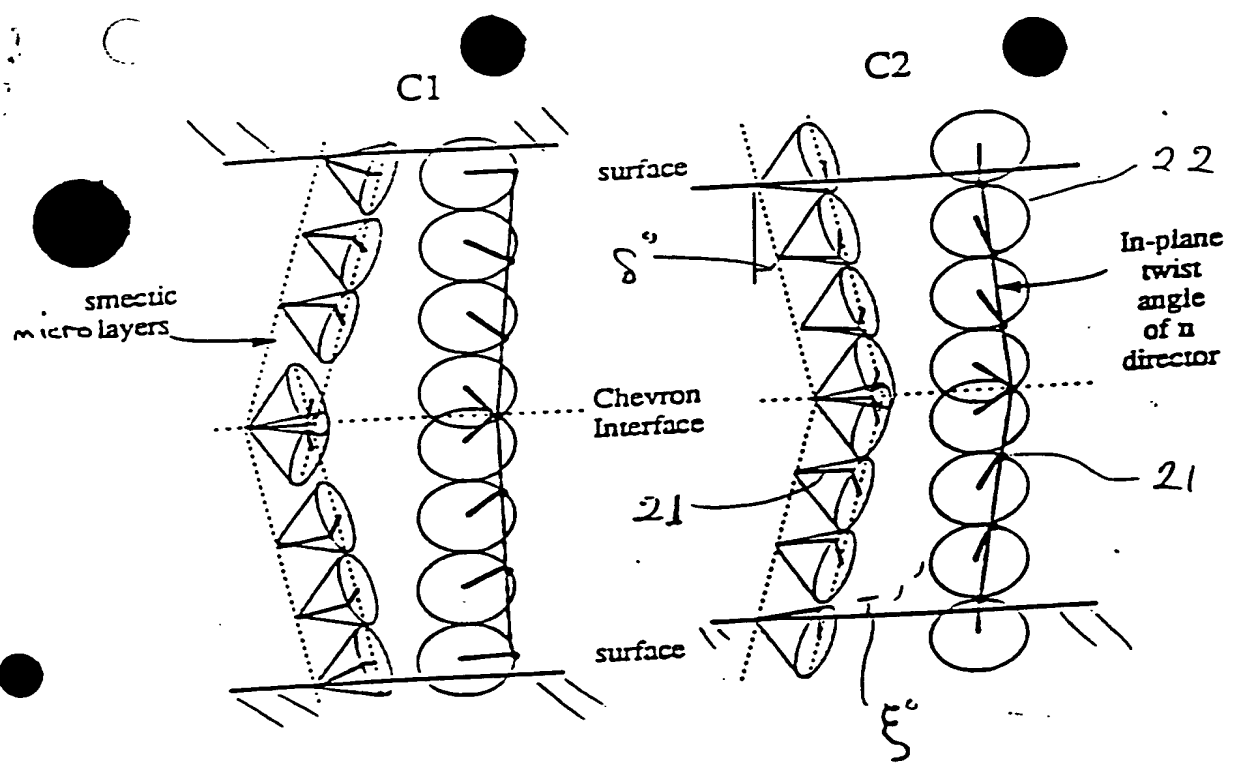
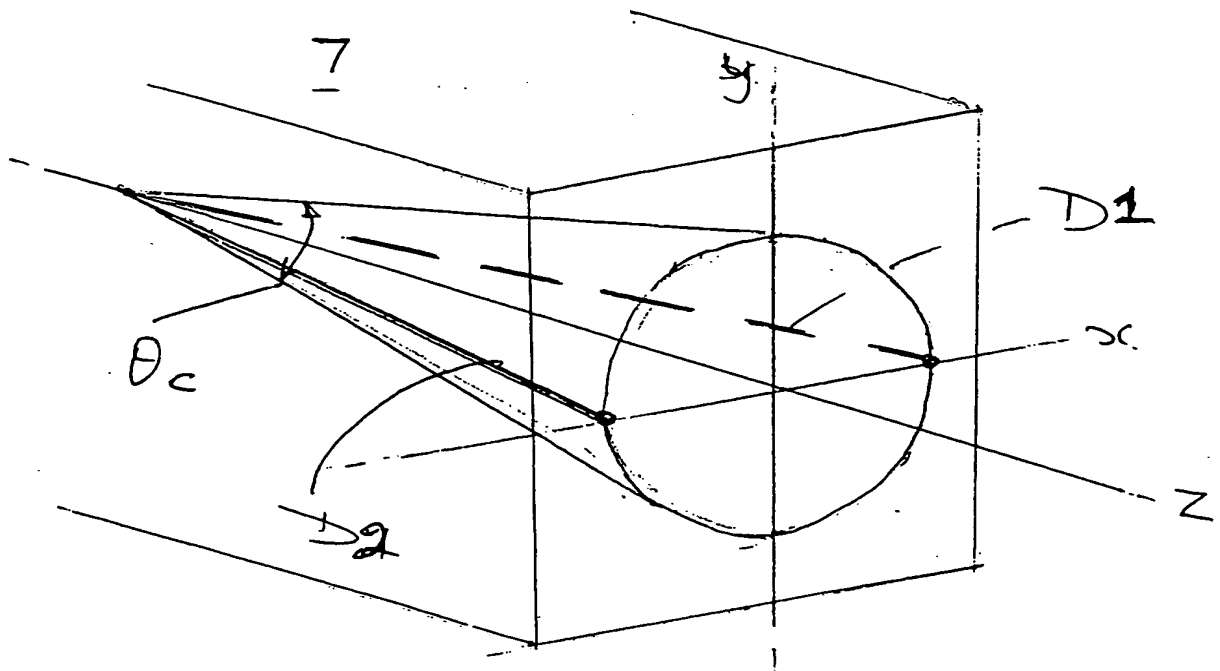
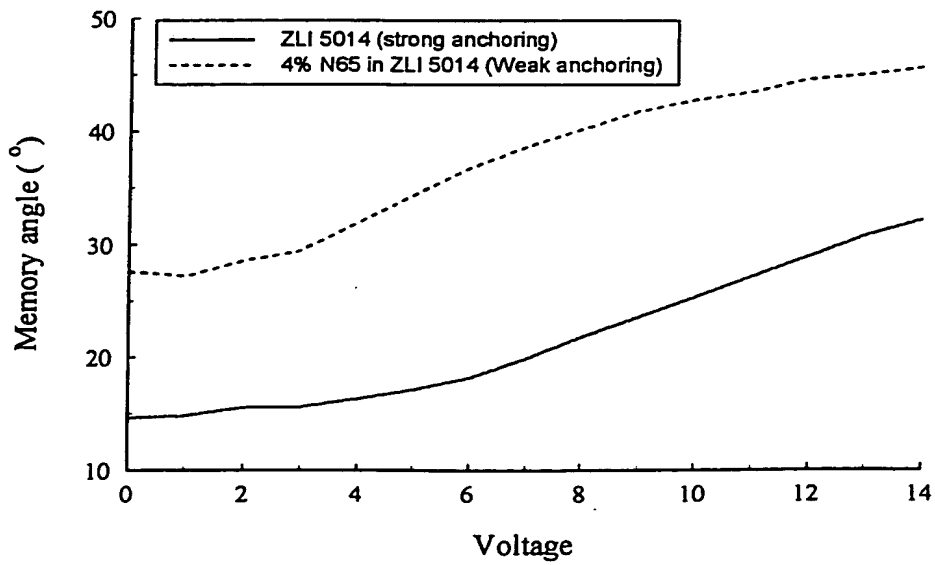


FIG 3





Fig 4Fig 5

PCT/GB 98 03011

Hewlett-Packard

8.10.98